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(54) Name of invention: Antibacterial fiber and manufacturing method thereof

(71) Applicant: 000001085
Kuraray Co., Ltd.
1621 Sakazu, Kurashiki-shi
Okayama-ken

(72) Inventor(s): Tadayoshi Kosen
Kuraray Co., Ltd.
892 Banchi Sakunichiichi
Nishi-koeda-shi
Ehime-ken

Kenichi Yoshioka
Kuraray Co., Ltd.
892 Banchi Sakunichiichi
Nishi-koeda-shi
Ehime-ken

(57) [Summary]

[Problem] An antibacterial fiber is proposed which is extremely good at preserving its antibacterial property over a long period of time.

[Solution] A polyester which is a mixture of inorganic fine particles containing metal ions is melt spun, and the spun yarn is cooled to a temperature below the glass-transition temperature. Next, it is run through a tubular heating device and subject to drawing under heat treatment; then, oil is applied, and the yarn is wound at a wind-up speed of 4000m/min or higher.

[Scope of patent claims]

[Claim 1] A type of antibacterial fiber, characterized by the following facts: the antibacterial fiber is a synthetic fiber which has a fiber-forming polymer containing 0.5-10 wt% of inorganic fine particles holding metal ions with an antibacterial function present in at least a portion of the surface of the fiber; in the following listed antibacterial test, after 150 washing cycles, the bacteria reducing rate of pneumobacilli is 80% or greater.

- The fiber sample is loaded into a washing machine containing 40 L of water at 40°C; after adding 80 g of a neutral detergent and washing for 5 minutes, rinsing is performed for 3 cycles, followed by dewatering and drying; with aforementioned operations taken as one cycle, 150 cycles are performed repeatedly; for the obtained fiber sample, the following formula is used to derive the bacteria-reducing rate (%) for pneumobacilli using the shake flask method defined by the Council of Fiber Product Hygiene Processing:

$$\text{Bacteria-reducing rate (\%)} = \{(N_0 - N_1) / N_0\} \times 100$$

N_0 = Number of pneumobacilli applied on the feed fiber sample.

N_1 = Number of pneumobacilli surviving on the feed fiber sample at end time of the antibacterial property test.

[Claim 2] The antibacterial fiber contained in Claim 1, characterized by the fact that the fiber-forming polymer is a polyester.

[Claim 3] A manufacturing method of the antibacterial fiber described in Claim 1, characterized by the following facts: inorganic fine particles holding metal ions in them are mixed into the fiber-forming polymer after completion of polymerization in any of the steps before said polymer is spun from the spinning nozzle; melt spinning is performed; the spun yarn is cooled to a temperature below the glass-transition temperature of the fiber-forming polymer; then it is made to run in a tubular heating device and is subjected to drawing under heat treatment; then, oil is applied, and the yarn is wound up at a wind-up speed of 4000 m/min or higher.

[Claim 4] A fiber product, manufactured from the antibacterial fiber described in Claim 1.

[Background of invention]

[0001]

[Field of invention] The present invention pertains to antibacterial fibers and manufacturing methods thereof; specifically, this invention pertains to dyes, post-processing and post-treatment washing and the like, laundry, is concerned with not diminishing the antibacterial property through bathing and use,

and is related to an antibacterial fiber which is extremely good at preserving its antibacterial property over a long period of time and the manufacturing method thereof, which in the past has not existed.

[0002]

[Prior art] There are various microorganisms and bacteria which live in environments inhabited by humans, attaching to and flourishing on the skin, clothes, and resulting in various disorders such as breathing and dermatological problems. A degradation and deterioration in the quality of clothing products and foul odors also occur. In particular, when compared to natural fibers, the sweat absorbing characteristics of synthetic fibers are lower. Therefore, when clothing made of synthetic fibers are worn, this easily allows an environment to be created where microbes attach to, flourish, and decay in the sweat on skin and clothes, generating sweat odors. Since the past, this has created demand for, and various types of research and development surrounding a synthetic fiber with a clean antibacterial characteristic which is safe and comfortable to wear and does not produce any foul smelling odors.

[0003] There was a period of time when silver compounds and mercury compounds were used to provide fibers with their antibacterial characteristic, however, the toxicity of these compounds poses a problem; the great majority of these compounds having been banned from use. Also, there has been proposed (Unexamined patent application publication S57-51874) a carpet manufactured from fibers with antifungal and antibacterial characteristics according to the post-treatment of No. 4 grade ammonium salts from silicone containing highly safe antifungal and antibacterial agents. Although the No. 4 grade ammonium salts from silicone have reactions and affinities with cellulose fibers and display antibacterial effectiveness in terms of washing durability characteristics, with synthetic fibers the reactions and affinities are less preferable, and so the antibacterial function is merely temporary and the durability nonexistent.

[0004] Further, a method for manufacturing fibers is proposed (Unexamined patent application publication S54-147220) whereby the metal compounds dissolved and extracted from the metal ions of zinc, copper, and silver, which are known from the past for their antibacterial characteristics, are mixed within the fiber-forming polymer. However, the metal compounds from cases based on this method greatly effect the fiber-forming polymer; for example, the additive ratios are significantly limited, there is a decline in passage through the fiber-producing operations, individual strands break while the yarn is spun, the pack filter is clogged reducing pack life, and shags occur more frequently during drawing. Moreover, by directly mixing the metal compounds as is into the fiber-forming polymer, there are cases according to this method where the amount of metal ions on the surface of the fiber is reduced with usage and the passage of time. This accompanies a significant reduction in the

duration of the antibacterial characteristic, complicating the preservation of an exceptional antibacterial function over a long period of time.

[0005] Furthermore, there is a method proposed (Examined patent application publication S63-54013, Unexamined patent application publication S63-175117) whereby fibers are formed by kneading zeolite holding such metal ions as silver, copper, and the like, into the fiber-forming polymer. Cases based on this method have also resulted in decreases in the amount of metal ions that exist on the surface portion of the fibers with the passage of time and with usage. This accompanies a gradual decrease in the antibacterial function, and the inability to obtain an antibacterial fiber with a durability characteristic.

[0006]

[Problem addressed by invention] The present invention proposes an antibacterial fiber and the manufactured goods thereof which have exceptional durability and maintain high antibacterial characteristics, even after having been subject to long periods of dye processing, washing, post-processing, post-treatment, bathing, usage, and the like.

[0007]

[Means for solving problem] The present inventors have observed and arrived at the present invention based on the results of extensive investigations into mixing inorganic fine particles holding metal ions into a fiber-forming polymer, and after spinning the fibers and making cloth using non-contact heat treatment drawing methods, it is then expected that an antibacterial property and respective durability characteristic can be acquired. According to this invention, while the thread is spun, fiber microstructures containing loose non-crystallized sections are formed, and not only do the metal ions near the fiber surface move toward the surface but so do the metal ions in the center of the fiber, and so it can be ascertained that the antibacterial property will endure. The antibacterial fiber of this invention, is namely a synthetic fiber which has a fiber-forming polymer containing 0.5~10 wt% of inorganic fine particles holding metal ions with antibacterial function present in at least a portion of the surface of the fiber; in the following listed antibacterial test, after 150 washing cycles, the bacteria-reducing rate of pneumobacilli is 80% or higher.

- The fiber sample is loaded into a washing machine containing 40 L of water at 40°C; after adding 80 g of a neutral detergent and washing for 5 minutes, rinsing is performed for 3 cycles, followed by dewatering and drying; with aforementioned operations taken as one cycle, 150 cycles are performed repeatedly; for the obtained fiber sample, the following formula is used to derive the bacteria reducing rate (%) for pneumobacilli using the shake flask method defined by the Council of Fiber Product

Hygiene Processing:

Bacteria-reducing rate (%) = $\{(N_0 - N_1)/N_0\} \times 100$

N_0 = Number of pneumobacilli applied on the feed fiber sample.

N_1 = Number of pneumobacilli surviving on the feed fiber sample at end time of the antibacterial property test.

In addition, the antibacterial fiber of the present invention is characterized by mixing inorganic fine particles holding metal ions in them into the fiber-forming polymer after completion of polymerization in any of the steps before said polymer is spun from the spinning nozzle; melt spinning is performed; the spun yarn is cooled to a temperature below the glass-transition temperature of the fiber-forming polymer; then it is made to run in a tubular heating device and is subjected to drawing under heat treatment; then, oil is applied, and the yarn is wound up at a wind-up speed of 4000 m/min or higher.

[0008] Furthermore, the goods and finished products manufactured from the aforementioned antibacterial organic polymer fiber are included in the present invention, such as threads, fabrics, clothing, bedding material, curtains, carpets, baskets, towels, medical supplies such as bandage gauze, masks, and the like.

[0009] Examples of fiber-forming polymers consisting of antibacterial fibers of the present invention are thermal fusion polymers such as, fiber-forming polyesters, polyamides, polyolefin, chlorovinyl, chlorovinylidene, and the like. Even among this group are thermal plastic polymers which can be melt spun such as, polyesters, polyamides, and the like. It is desirable to melt spin these thermal plastic polymers and be able to manufacture fibers containing inorganic fine particles having antibacterial metal ions.

[0010] Further, the metal ions of the present invention having antibacterial characteristics include, silver, copper, zinc, lead, chrome, iron, nickel, mercury, and the like. It is preferable to maintain only 1 type or 2 or more types of these metal ions with the inorganic fine particles. In particular, it is desirable to use silver as the metal ion in the present invention as the antibacterial characteristic will continue for a long period of time.

[0011] There is no particular restriction to the types of metal ions held by the inorganic fine particles. Any substance which does not exhibit active degradation of the organic polymer can be used. Substances which have a high antibacterial metal ion maintainability and capacity for exchanging ions or absorbing metal ions are preferred. Examples of these types of inorganic fine particles include, zeolite, zirconium phosphate, calcium phosphate, etc. When zeolite is used it is particularly necessary

to sufficiently heat and dry the zeolite and keep the moisture ratio down. If there is a high zeolite moisture ratio, then the ability to pull the fiber-forming organic polymer of poyesters, and the like, worsens. Even if it is possible to temporarily spin the yarn, there is a significant decrease in strength of the fibers obtained, and so it is necessary to use caution. At this time, a temperature above 500°C is preferred for the heating and drying treatment of the zeolite.

[0012] As for the inorganic fine particles, an average particle diameter of 0.1~5 μ m is preferred, and 0.3~2 μ m is even better preferred. If the inorganic fine particle is smaller than 0.1 μ m, clumping among the fine particles easily occurs when the fine particles in the polymer are dispersed. Moreover, when the yarn is spun, the filter becomes clogged, and snags easily occur during drawing. On the other hand, if the inorganic fine particle size is larger than 5 μ m, then the filter will clog or threads will break during yarn spinning, and the yarn spinning process will be unsatisfactory.

[0013] As for the inorganic fine particles holding metal ions with antibacterial characteristics (hereinafter to be referred to as "antibacterial inorganic fine particles"), the higher the concentration of antibacterial metal ions, the better. For example, it is advantageous for the inorganic fine particles to have an ion exchange capacity such as zeolite, where over 90% of the ion exchange capacity is devoted to the antibacterial metal ions; or, when the metal ions are held using the physical absorbing capacity of the inorganic fine particles, it is preferable to have more than 90% absorbed while the metal ions are being absorbed during saturation.

[0014] The antibacterial inorganic particles are normally obtained through drying after the impregnation process of the inorganic fine particles using the liquid of the aqueous solution containing the aforementioned types of antibacterial metal ions. There no particular restriction to the manufacturing methods for antibacterial inorganic fine particles with regards to the present invention. Inorganic fine particles which hold a high concentration of antibacterial metal ions can always be used.

[0015] The preferred additive amount for antibacterial inorganic fine particles, based on the weights of fiber-forming polymers, is 0.5~10 wt%; 1~5 wt% is better preferred. Although it depends on both the ion exchange capacity or the absorption amount according to the antibacterial metal ions of the inorganic fine particles, and even if more than 90% of the ion exchange capacity or the metal ion absorption ability uses the ions exchanged with the antibacterial metal ions, or the absorbed inorganic fine particles, then it is difficult to provide an adequate antibacterial characteristic if there is less than 0.01 wt% of the additive amount for the antibacterial inorganic fine particles; in particular, an antibacterial characteristic with a durability characteristic is difficult to obtain. On the other hand, if

10 wt% is exceeded, then the antibacterial function will be sufficient, but during yarn spinning the ratio occupied by the inorganic fine particles in the polymer flow grows too large. The viscosity of the polymer flow decreases, the spun yarn pack becomes clogged, and thus, the fiber-forming process easily deteriorates. Moreover, it is not economical to use large amounts of expensive antibacterial inorganic fine particles.

[0016] As for the additive method for the antibacterial inorganic fine particles, considering the effects of the respective components during the polymerization reaction, it is preferable to add to the fiber-forming polymer after completion of polymerization. Accordingly, directly after polymerization of the fiber-forming polymer, it is appropriate to adopt the additive method for antibacterial inorganic fine particles at any stage up until the polymer is spun from the spinning nozzle while yarn spinning is performed. This is done using polymer powder, pellets, chips, and the like, and takes place during melting and kneading for manufacturing pellets and chips from the fiber-forming polymers only at the completion of polymerization. As for the method for adding antibacterial inorganic fine particles to the fiber-forming polymer which is made into cloth, antibacterial inorganic fine particles are mixed first with the types of low-quantity polymers similar to fiber-forming polymers. Afterward, master chips can be made by adding to the fiber-forming compound, or the yarn spinning method can be directly performed as is. In that case, low-quantity polymers become a dispersing medium, and the dispersing characteristic inside the fiber for the antibacterial inorganic fine particles can be further improved. However, in that case, it is necessary to be cautious of the amount of low-quantity polymer used. In particular, if the amount of low-quantity polymer with respect to the fiber-forming polymer is excessive, then the viscosity is reduced during the formation of fibers.

[0017] Furthermore, agents which can be added to the organic polymer fibers, in addition to the aforementioned antibacterial inorganic fine particles of the present invention, are used as needed and include, ultraviolet light absorbing agents, antioxidant agents, sliding agents, flame resistant agents, plasticity agents, pigments, and the like.

[0018] Next, the manufacturing method of the present invention will be explained. Inorganic fine particles holding metal ions in them are mixed into the fiber-forming polymer after completion of polymerization at any of the steps before said polymer is spun from the spinning nozzle, and melt spinning is performed. There are no particular restrictions for the melt spinning temperature, melt spinning speed, etc. The fibers can be manufactured under normal conditions using the fiber-forming polymers.

[0019] For example, the melt spinning temperature is set to a temperature 20~40°C higher than the

melting point of the fiber-forming polymer. The melt spinning speed (discharge amount) is roughly 2~50 g/single aperture 1mm²×min.

[0020] There are also no particular restrictions as to the size and number of the spun yard apertures, and for the spun yard nozzle shape of the spinning nozzle. The purpose is to be able to make adjustments with regard to the single fiber degree, general Tenier number, cross-sectional shape, etc., of the antibacterial fiber. Also, the melt spun thread filament is cooled to a temperature below the glass-transition temperature. As for the cooling methods and cooling devices in that case, it is preferable to have the methods and devices to be able to cool the melt spun thread filament below the glass-transition temperature. There are no particular restrictions, however, it is preferable to have a cool air blowing device such as a cool air blowing tube at the base of the spinning nozzle, where cool air is blown on the spun fibers and cooled below the glass-transition temperature. At that time, there are no particular restrictions for the cooling conditions such as the angle at which the cooling air is blown with respect to the spun thread filament, the humidity and temperature of the cooling air, and the speed at which the cool air is blown. It is preferable to have conditions whereby there is uniform cooling, and the speed of the thread filament spun from the spinning nozzle does not cause the thread to vibrate. Even within those conditions, it is preferable to smoothly obtain a high quality fiber by blowing cool air in the direction perpendicular to the direction of the spinning with respect to the spun thread filament, and setting the cooling air temperature to roughly 20~30°C, the humidity to 20~60%, and the wind or blowing speed to 0.4~1.0m/sec. Further, when using the cool air blowing tube to cool under the aforementioned conditions, it is preferable to have the cool air blowing tube approximately 50~200 cm in length, and to provide for either a slight gap or no gap directly beneath the spinning nozzle depending on the type of fiber-forming polymer used for forming fibers.

[0021] Next, the fiber thread filaments which are cooled below the glass-transition temperature are drawn uninterruptedly and as is directly into the heating region. The temperature of the heating region is attained differently according to the types of fiber-forming polymers used for forming fibers. However, in general, it is preferable for the temperature to be above the glass-transition temperature. For example, when using polyesters, it is desirable to satisfy the practical uses of the physical properties of the obtained polyester fibers by setting the temperature to 40°C above the glass-transition temperature; it is preferable to set the temperature 100°C above. It is preferable to set the upper temperature limit of the heating region to a temperature that prevents single strands from breaking, fusing, etc., within the fibers inside the heating region. Moreover, it is preferable to have a construction that can draw the fibers, increase the thread filament tensile strength, and generate

resistance between the thread filament that is run inside the heating region and the air that encompasses the thread filament. The setting position, heating range length, etc., from the spinning nozzle for the heating region can be adjusted appropriately according to the spinning amount and types of fiber-forming polymers used for producing fibers, the cooling temperature, the spinning speed, the heating range temperature, etc. However, it is desirable to be able to heat and smoothly and uniformly draw the fibers inside the heating range by setting the heating range length to approximately 1.0~2.0 m, and the distance from directly below the spinning nozzle to the entrance of the heating range to approximately 0.5~3 m.

[0022] In addition, after oil is applied as needed with regard to the fibers drawn in the heating range, the fibers are pulled at high speed. According to the present invention, it is necessary to have a fiber pulling speed of 4000 m/min or higher for the manufacturing operations of the drawn fibers from the aforementioned successive operations. If the pulling speed is less than 4000 m/min, then the fibers in the heating regions will not be adequately drawn, which will diminish the mechanical properties of the obtained fibers. Moreover, the methods of the present invention from the aforementioned successive operations will not be smoothly performed; in particular, there will be variation in the tensile strength of the thread filaments in the heating range, overheating, etc., which will make it difficult to carry out the drawing evenly. Further, there are loose fiber microstructures in the non-crystallized sections as the threads are drawn, in comparison to the conventional methods according to the fiber-forming methods of the present invention. As for the results, it is realized that this invention effectively promotes the migration of metal ions inside the fiber.

[0023] There are no particular restrictions for the cross-sectional shapes of the fibers with regard to the present invention. Various examples of preferred cross-sectional shapes, in addition to the normal circular cross-section, include elliptical shapes, triangular shapes, rectangular shapes, polygonal shapes, hollow shapes, multi-leafed shapes, arrays, V-shapes, T-shapes, etc. Further, even if there are conjugate fibers with the different fiber-forming polymers, or with the same fiber-forming polymers, it is acceptable, and there are no particular restrictions for the cross-sectional shape thereof, such as core/sheath, side-by-side, etc. However, for conjugate fibers, it is necessary to expose a minimum percentage of fiber-forming polymers containing antibacterial inorganic fine particles on the fiber surface. If the cross-section of the fiber is completely enclosed by the fiber-forming polymer, which does not contain antibacterial inorganic fine particles, and there is absolutely no exposure of the fiber-forming polymers containing antibacterial inorganic fine particles on the fiber surface, then there is a significant reduction in the antibacterial capacity, and from a practical use perspective the antibacterial

capacity will be unsatisfactory.

[0024] The antibacterial fiber of the present invention is effective against a variety of bacteria, such as, black fungus, blue fungus, bacillus subtilis, pseudomonas aeruginosa, bacillus coli, enteritis bipurio bacillus, salmonella, trichophyton, pneumobacilli, MRSA, and the like.

[0025] The fibers of the present invention can be used for such goods as, jackets, underwear, pajamas, abdominal wrap, work wear, aprons, inner soles for shoes, socks, carpets, strands used for mops, dust mat, futon, futon cover, pillow cover, bed, bed cover, blanket, sheets, bath mat, towel, cabinet towel, table cloth, curtain, shower curtain, net, door knob cover, wall paper, lab coat, surgical thread, surgical apparel, patient gown, bandage, adhesive backings, hats, gauze, masks, bed sore prevention mats, diaper cover, paper diaper, chart paper, slippers, tissue paper, wet tissue, tooth brush, gloves, various wipers, aprons, and filters for water filters, air filters, and the like. Products such as these can be provided with a durable and exceptional antibacterial characteristic.

[0026]

[Embodiments] The present invention is explained below according to its preferred embodiments, however, the scope of the present invention is not limited to these embodiments. The calculated values within the preferred embodiments are calculated based on the following methods.

[0027] (Antibacterial test) After using the thread obtained from actual embodiment and comparative examples to conduct a prescribed number of washing cycles using the HL (washing) treatment method shown below, the following formula (1) is used to derive the bacteria-reducing rate (%) for pneumobacilli using the shake flask method defined by the Council of Fiber Product Hygiene Processing:

$$\text{Bacteria-reducing rate (\%)} = \{(N_0 - N_1) / N_0\} \times 100 \quad (1)$$

N_0 = Number of pneumobacilli applied on the feed fiber sample.

N_1 = Number of pneumobacilli surviving on the feed fiber sample at end time of the antibacterial property test.

HL (washing) treatment: The fiber sample is loaded in a washing machine containing 40 L of water at 40°C; after adding 80 g of neutral detergent and washing for 5 min, rinsing is performed for 3 cycles, followed by dewatering and drying.

[0028] Embodiment 1

Polyethylene terephthate is made into fibers with a limiting viscosity $[\eta] = 0.68$ and a 2 wt% additive of zirconium phosphate holding mercury ions (average particle diameter 0.2 μm , ion exchange rate 90%) as the antibacterial inorganic fine particles; the spun yarn temperature is 285°C; the tube heater

temperature is 200°C; the pulling speed is 4500m/min; and drawn thread is obtained (Table 1, Table 2) with an acceptable process capability of 75d/36f. The results as shown in Table 2 confirm a favorable antibacterial characteristic and durability characteristic thereof.

[0029]

Table 1

	Brand (d/f)	Antibacterial inorganic fine particles					Fiber shape	Combined ratio	Fiber- forming polymer
		Base material	Particle diameter (μ m)	Metal ion	Ion exchange rate (%)	Additive amount (wt%)			
Embodiment 1	75/36	Zirconium phosphate	0.2	Ag	90	2	Single	--	PET
Embodiment 2	"	"	"	"	90	5	"	--	"
Embodiment 3	150/86	"	"	Ag+Cu	85	3	"	--	"
Embodiment 4	"	"	"	Ag+Zn	85	5	"	--	"
Embodiment 5	"	"	"	Ag	90	2	"	--	Nylon
Embodiment 6	75/36	Zeolite	1.0	"	"	2	"	--	PET
Embodiment 7	"	Zirconium phosphate	0.2	"	"	2 (in sheath amount)	Core/ Sheath	1/1	Core PET Sheath Nylon
Embodiment 8	"	Zeolite	1.0	"	"	3 (in PET)	Side by side	1/1	PET/Nylon
Comp. example 1	"	Zirconium phosphate	0.2	"	"	0.1	Single	--	PET
Comp. example 2	"	"	"	"	"	1.5	"	--	"
Comp. example 3	"	"	"	"	"	2	"	--	"
Comp. example 4	"	"	"	"	"	3 (in core amount)	Core/ Sheath	1/1	Core PET Sheath Nylon
Comp. example 5	"	"	"	"	"	2	"	--	PET

	Spun yarn conditions			Process capability	Bacteria-reducing rate			Notes
	Spun yarn temperature (°C)	Tube heater temperature (°C)	Pulling speed (m/min)		Washing 10 cycles	Washing 50 cycles	Washing 160 cycles	
Embodiment 1	285	200	4500	o	99	95	88	
Embodiment 2	"	"	5000	o	99	98	92	
Embodiment 3	280	180	"	o	99	90	80	
Embodiment 4	"	200	"	o	99	92	80	
Embodiment 5	260	180	4800	o	99	99	95	
Embodiment 6	285	200	4000	o	99	90	85	
Embodiment 7	280	"	"	o	99	95	90	
Embodiment 8	"	180	4500	o	99	95	90	
Comp. example 1	285	200	"	o	85	40	--	
Comp. example 2	"	"	"	x	--	--	--	
Comp. example 3	"	"	3400	Δ	--	--	--	Physical defect
Comp. example 4	"	"	4000	o	10	5	--	
Comp. example 5	"	2 step method		o	99	80	50	

[0030] Embodiments 2~4

The thread was produced in the same manner as Embodiment 1, except the amounts of antibacterial inorganic fine particle additive in the fiber and types of antibacterial constituents were varied. At any rate, an acceptable process capability for thread drawing of 75d/36f and 50d/36f was obtained (Table 1, Table 2). The results of the antibacterial evaluation at that time are shown in Table 2.

[0031] Embodiment 5

The thread is produced in the same manner as Embodiment 1, except nylon is used as the fiber-forming polymer. An acceptable process capability for thread drawing of 50d/36f was obtained (Table 1, Table 2). The results of the antibacterial evaluation at that time are shown in Table 2.

[0032] Embodiment 6

The thread was produced in the same manner as Embodiment 1, except zeolite was used as the base material for the antibacterial inorganic fine particles. An acceptable process capability for thread drawing of 75d/36f was obtained (Table 1, Table 2). The results of the antibacterial evaluation at that time are shown in Table 2.

[0033] Embodiment 7

The thread was produced in the same manner as Embodiment 1, except polyethylene terephthate with $[\eta]=0.68$ and a core/sheath compound fiber using nylon 6 with a molecular weight of 13000 and with a 2 wt% additive amount of zirconium phosphate holding mercury metal ions in the core were used. An acceptable process capability for thread drawing of 75d/36f was obtained (Table 1, Table 2). The results of the antibacterial evaluation at that time are shown in Table 2.

[0034] Embodiment 8

The thread was produced in the same manner as Embodiment 1, except a side-by-side type and nylon 6 with a molecular weight of 13000 and polyethylene terephthate with $[\eta]=0.68$ and with a 3 wt% additive amount of zeolite holding mercury ions were arranged. An acceptable process capability for thread drawing of 75d/36f was obtained (Table 1, Table 2). The results of the antibacterial evaluation at that time are shown in Table 2.

[0035] Comparative example 1

The thread was produced in the same manner as Embodiment 1, except a 0.1 wt% additive amount of

zirconium phosphate holding mercury ions as the antibacterial inorganic fine particles in the polyethylene terephthalate was used. The process capability was favorable, however, was not good when compared with the embodiments.

[0036] Comparative example 2

The thread was produced in the same manner as Embodiment 1, except a 15 wt% additive amount of zirconium phosphate holding mercury ions as the antibacterial inorganic fine particles in the polyethylene terephthalate was used. There was a large decrease in the viscosity of the polyethylene terephthalate, and due to the poor thread pulling, a satisfactory process capability was not attained (Table 1, Table 2).

[0037] Comparative example 3

The thread was produced in the same manner as Embodiment 1, except a spun yard speed of 3400 m/min was used, but resulted in difficult drawing. There were several instances of broken threads, and an increase in physical elasticity, making its use in a practical sense poor.

[0038] Comparative example 4

The thread was produced in the same manner as Embodiment 7, except the core/sheath fibers used nylon 6 with a molecular weight of 13000 for the sheath, and polyethylene terephthalate with $[\eta]=0.68$ and 3 %wt additive amount of zirconium phosphate holding mercury ions for the core. The process capability was favorable, however, it was significantly inferior when compared with the embodiments.

[0039] Comparative example 5

The antibacterial inorganic fine particles and the fiber-forming polymer are the same as in Embodiment 1, and the thread producing method spins and collects thread at 1000 m/min. The conventional 2 step method was used in the post drawing process, whereby a thread drawing process capability of 75d/36f was obtained. This process capability was favorable, and both the antibacterial evaluation and initial performance were exceptional, however, the durability characteristic was inferior to the present invention.

[0040] Conclusion

The process capability, antibacterial function, and durability characteristic thereof of the present invention are extremely favorable. However, as shown in the comparative examples, the effectiveness is insufficient when there is not enough antibacterial constituent, and the process capability is worsened when the antibacterial constituent is increased. Also, the effectiveness of the antibacterial constituent is poor, when the antibacterial constituent is not present in the fiber surface. In addition, although the extent of the durability characteristic of the antibacterial function is recognized with

regard to conventional thread producing methods, it has been acknowledged that the thread producing methods of the present invention offer further improvements in the durability characteristic of the antibacterial fibers obtained thereof.

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(71) 出願人 000001065

株式会社クラレ

岡山県倉敷市酒津1621番地

(72) 発明者 古泉 忠由

愛媛県西条市期日市892番地 株式会社ク

ラレ内

(72) 発明者 吉岡 謙一

愛媛県西条市期日市892番地 株式会社ク

ラレ内

(54) 【発明の名称】 抗菌性繊維及びその製造方法

(57) 【要約】

【課題】 長期間にわたり極めて良好な抗菌性を保持することが出来る抗菌性繊維を提供する。

【解決手段】 銀イオンを保持させた無機微粒子を配合したポリエステルを熔融紡出し、紡出糸条を一旦繊維形成性ポリマーのガラス転移温度以下まで冷却し、次いでチューブ型加熱装置内を走行させて延伸熱処理した後、油剤を付与し4000m/分以上の引取速度で巻取る。

【特許請求の範囲】

【請求項1】 抗菌作用を有する金属イオンを保持させた無機微粒子を0.5〜10重量%含有する繊維形成性重合体が繊維表面の少なくとも一部に存在している合成繊維であって、下記の抗菌試験による150回の洗濯後の肺炎桿菌の減菌率が80%以上であることを特徴とする抗菌性繊維。

・繊維を、温度40℃の水40リットルを入れた洗濯機に投入して、中性洗剤80gを加えて、5分間洗濯した後、すすぎを3回行い、脱水乾燥する処理を1回の洗濯とし、これを150回繰り返した後の繊維について、繊維製品衛生加工協議会で定めたシェークンラスコ法により菌種として肺炎桿菌を使い、下記式により減菌率(%)を求める。

$$\text{減菌率}(\%) = \{(N_0 - N_1) / N_0\} \times 100$$

N_0 = 原綿に施した肺炎桿菌の数

N_1 = 抗菌性試験終了時に原綿中で生存していた肺炎桿菌の数

【請求項2】 繊維形成性重合体がポリエステルである請求項1記載の抗菌性繊維。

【請求項3】 重合完了後の繊維形成性重合体中に、該重合体が紡糸口金から紡出されるまでの任意の段階で金属イオンを保持させた無機微粒子を混合して、浴融紡出し、紡出糸条を一旦繊維形成性ポリマーのガラス転移温度以下まで冷却し、次いでチューブ型加熱装置内を走行させて延伸熱処理した後、油剤を付与し4000m/分以上の引取速度で巻取することを特徴とする請求項1記載の抗菌性繊維の製造方法。

【請求項4】 請求項1の抗菌性繊維から製造された繊維製品。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は抗菌性繊維およびその製造方法に関する。詳細には、本発明は染色、洗浄などの後加工や後処理、洗濯、着用や使用などを経ても抗菌性が失われず、長期間にわたり従来にない程極めて良好な抗菌性を保持することが出来る抗菌性繊維及びその製造方法に関するものである。

【0002】

【従来の技術】 人間の生活環境下には種々の細菌類やカビなどが棲息しており、人体、繊維製品などに付着して繁殖し、皮膚障害や喘息などの様々の疾病を引き起こしたり、繊維製品の劣化や劣化、または悪臭の発生をもたらしている。特に合成繊維は天然繊維に比べて吸汗性が低いために、合成繊維製の衣類を身につけた場合には、汗の付着した皮膚や衣類等に微生物が付着し繁殖して腐敗現象を起こし易く、汗くさい臭いを生ずる。そのため悪臭を発生せず、快適で安全な清潔感のある抗菌性のある合成繊維が古くから求められており、そのための研究開発が従来から色々行われている。

【0003】 繊維に抗菌性を付与するために有機銅化合物や有機水銀化合物が繊維に対して用いられていた時期があるが、これらの化合物の毒性が問題となり、その大半が現在使用中止となっている。また安全性の高い抗菌・防カビ剤であるシリコン系の第4級アンモニウム塩などを後処理によって繊維に付着させて抗菌・防カビ性のカーベットを製造することが提案されている（特開昭57-51874号公報）。しかし、シリコン系の第4級アンモニウム塩はセルロース系繊維には反応性や親和性を有し洗濯耐久性のある抗菌効果を示すが、合成繊維に対しては反応性または親和性に劣るためその抗菌作用は一時的なものに過ぎず耐久性がない。

【0004】 また、抗菌性を有することが古くから知られている銀、銅、亜鉛等の金属イオンを溶出させ得る金属化合物を繊維形成性重合体中に混合して繊維を製造する方法が提案されている（特開昭54-147220号公報）。しかし、この方法による場合はそれらの金属化合物が繊維形成性重合体に及ぼす影響が大きく、添加割合が著しく制限されたり、繊維化工程での工程通過性が低下し、特に紡糸時の単糸切れ、バックフィルターの目詰まりによるバック寿命の低下、延伸時の毛羽の頻発などを生じ易い。しかも、金属化合物を単にそのまま直接重合体中に配合しているこの方法による場合は繊維表面に存在する金属イオン量が時間の経過や使用に伴って減少してゆくにつれて抗菌性能が短時間に著しく低下し、長時間にわたって優れた抗菌作用を維持することが困難であった。

【0005】 更に、銀、銅等の金属イオンを保持させたゼオライトを繊維形成性重合体中に練り込んで繊維を形成する方法が提案されているが（特公昭63-54013号公報、特開昭63-175117号公報）、この方法による場合も時間の経過や使用に伴って繊維表面部分に存在する金属イオンの量が低減してゆき、それに伴って抗菌作用も徐々に低下し、耐久性のある抗菌性繊維が得られない。

【0006】

【発明が解決しようとする課題】 本発明の課題は、染色加工や水洗などの後加工や後処理、洗濯、長時間使用の着用や使用などを経た後も、高い抗菌性を保ち得る耐久性に極めて優れた抗菌性繊維およびそれから成る繊維製品を提供することである。

【0007】

【課題を解決するための手段】 本発明者らは、上記の課題を解決すべく鋭意検討した結果、金属イオンを保持させた無機微粒子を繊維形成性重合体中に混合させて紡出したあと非接触熱処理延伸法により製糸化することにより、期待する抗菌性能とその耐久性を付与することができると見出して本発明に到達した。本発明によって延伸糸でありながらルーズな非品部を有する繊維微細構造が形成され、繊維表面付近に存在する金属イオンのみ

ならず繊維中心部に存在する金属イオンの繊維表面への移動を可能にし、抗菌性能が持続するものであると考えられる。すなわち、本発明は、抗菌作用を有する金属イオンを保持させた無機微粒子を0.5~10重量%含有する繊維形成性重合体が繊維表面の少なくとも一部に存在している合成繊維であって、下記の抗菌試験による150回の洗濯後の肺炎桿菌の滅菌率が80%以上であることを特徴とする抗菌性繊維である。

・繊維を、温度40℃の水40リットルを入れた洗濯機に投入して、中性洗剤80gを加えて、5分間洗濯した後、すすぎを3回行い、脱水乾燥する処理を1回の洗濯とし、これを150回繰り返した後の繊維について、繊維製品衛生加工協議会で定めたシェークフラスコ法により菌種として肺炎桿菌を使い、下記式により滅菌率(%)を求める。

$$\text{滅菌率}(\%) = \{(N_0 - N_1) / N_0\} \times 100$$

N_0 = 原綿に施した肺炎桿菌の数

N_1 = 抗菌性試験終了時に原綿中で生存していた肺炎桿菌の数

また、本発明の抗菌性繊維は、重合完了後の繊維形成性重合体中に、該重合体が紡糸口から紡出されるまでの任意の段階で金属イオンを保持させた無機微粒子を混合して、溶融紡出し、紡出糸条を一旦繊維形成性ポリマーのガラス転移温度以下まで冷却し、次いでチューブ型加熱装置内を走行させて延伸熱処理した後、油剤を付与し4000m/分以上の引取速度で巻取ることにより得られる。

【0008】更に、本発明は上記の抗菌性有機重合体繊維から製造された繊維製品を包含し、そのような繊維製品としては、糸、布帛、更には衣類、寝具、カーテン、カーペット、バスマット、タオル、包帯やガーゼ、マスクなどの医療品などの最終製品を含む。

【0009】本発明の抗菌性繊維を構成する繊維形成性重合体としては、例えば、繊維形成性のポリエステル、ポリアミド、ポリオレフィン、塩化ビニル、塩化ビニリデン等の熱溶解性重合体などを挙げることができ、それらのうちでも溶融紡糸が可能なポリエステル、ポリアミド等の熱可塑性重合体が抗菌性金属イオン保持無機微粒子を含有する繊維を溶融紡糸により簡単に製造することができ望ましい。

【0010】また、本発明において、抗菌性を有する金属イオンとは、銀、銅、亜鉛、鉛、クロム、鉄、ニッケル、水銀などの金属イオンをいい、無機微粒子にはこれらの金属イオンの1種類のみを保持させても、または2種以上を保持させても良い。特に本発明においては、銀イオンを使用すると抗菌性が長時間持続し望ましい。

【0011】金属イオンを保持させる無機微粒子の種類は特に制限されず、有機重合体繊維の劣化作用等を示さないものはいずれも使用でき、イオン交換能や金属イオン吸着能を有して抗菌性金属イオンの保持能の高い

ものが好ましい。そのような無機微粒子の例としては、ゼオライト、リン酸ジルコニウム、リン酸カルシウムなどを挙げることができる。特にゼオライトを使用する場合には、ゼオライトを十分に加熱乾燥して水分率を低く抑えておくことが必要であり、ゼオライトの水分率が高いと、ポリエステルなどの繊維形成性有機重合体の収率が悪くなり、仮に紡糸ができて得られる繊維の強度低下が著しくなるので注意を要する。この時のゼオライトの加熱乾燥処理は500℃以上の温度で行うことが好ましい。

【0012】そして無機微粒子としては、平均粒径が0.1~5μmのものが好ましく、0.3~2μmがより好ましい。無機微粒子が0.1μmよりも小さいと、重合体中に分散させる際に微粒子の凝集が生じ易くなり、しかも紡糸時にフィルターの日詰まりを生じたり、延伸により毛羽を生じ易くなる。一方、無機微粒子が5μmより大きいと、やはり紡糸時にフィルターの日詰まりや断糸等を生じて紡糸時の工程性が不良になり易い。

【0013】抗菌性を有する金属イオンを保持させた無機微粒子(以後「抗菌性無機微粒子」と云う)としては、抗菌性金属イオンをより高濃度で保持しているものが良く、例えば無機微粒子がイオン交換能を有するゼオライト等からなる場合は、そのイオン交換容量の90%以上が抗菌性金属イオンでイオン交換されているものが、また金属イオンが無機微粒子の物理的な吸着能により保持されている場合には飽和時の90%以上になるように金属イオンを吸着しているのが良い。

【0014】抗菌性無機微粒子は、通常、上記の様な抗菌性金属イオンを含む水溶液などの溶液で無機微粒子を含浸処理した後乾燥することにより得られるが、本発明においては抗菌性無機微粒子の製造方法は特に限定されず、抗菌性金属イオンを高濃度で保持している無機微粒子はいずれも使用できる。

【0015】抗菌性無機微粒子の添加量は、繊維形成性重合体の重量に基づいて0.5~10重量%にするのが好ましく、1~5重量%がより好ましい。無機微粒子における抗菌性金属イオンによるイオン交換容量または吸着量にもよるが、イオン交換容量または金属イオン吸着能の90%以上が抗菌性の金属イオンでイオン交換または吸着されている無機微粒子を使用する場合であっても、抗菌性無機微粒子の添加量が0.01重量%より少ないと繊維に充分な抗菌性を付与しにくく、特に耐久性のある抗菌性が得られにくくなる。一方、10重量%を超えると抗菌性能は充分であるが、紡糸時に重合体流中に無機微粒子の占める割合が大きくなりすぎて、重合体流の粘度低下、紡糸バックの日詰まりなどにより繊維化工程性が低下しやすくなり、しかも高価な抗菌性無機微粒子を多量に使用することになり経済的でない。

【0016】抗菌性無機微粒子の添加方法としては、重合反応時におけるそれらの成分の影響を考えると、重合

が完了した後の繊維形成性重合体に加えるのが良い。そのため、本発明では、抗菌性無機微粒子を、繊維形成性重合体の重合直後、重合済みの繊維形成性重合体からベレットやチップを製造するための溶融混練時、重合体粒末、ベレット、チップなどを用いて紡糸を行う際に重合体が紡糸口金から紡出されるまでの任意の段階などで添加する方法など適宜採用できる。更に製糸化する繊維形成性重合体に抗菌性無機微粒子を添加する方法として、繊維形成性重合体と同種の低分子量重合体に先に抗菌性無機微粒子を混合しておき、その後繊維形成性重合体に添加しマスターチップ化あるいは、そのまま直接紡糸する方法をとることができる。その場合には低分子量重合体が分散媒となり抗菌性無機微粒子の繊維内への分散性を一層向上させることができる。ただしその場合には低分子量重合体の使用量に注意する必要がある。特に繊維形成性重合体に対して低分子量重合体の量が多すぎると繊維化時粘度低下をまねき望ましい。

【0017】また本発明では上記の抗菌性無機微粒子の他に、必要に応じて有機重合体繊維に通常使用されている紫外線吸収剤、酸化防止剤、滑剤、難燃剤、可塑剤、染料などの他の添加剤を使用しても良い。

【0018】次に本発明の製造方法について説明する。重合完了後の繊維形成性重合体中に、該重合体が紡糸口金から紡出されるまでの任意の段階で金属イオンを保持させた無機微粒子を混合して、溶融紡出する。この場合の溶融紡出温度、溶融紡出速度などはとくに限定されず、繊維形成性重合体を用いて繊維を製造するのに通常使用されている条件下で行うことができる。

【0019】例えば溶融紡出温度は、繊維形成性重合体の融点より20～40℃高い温度に設定し、溶融紡出速度(吐出量)は約20～50g/単孔1mm²・分程度であるのが良い。

【0020】また紡糸口金における紡糸孔の大きさや数、紡糸孔の形状なども特に限定されず、目的とする抗菌性繊維の単繊維、総合デニール数、断面形状などに応じて調節することができる。そして溶融紡出した糸条は、一旦そのガラス転移点温度以下の温度に冷却する。その場合の冷却方法や冷却装置としては紡出した糸条をそのガラス転移点温度以下の温度に冷却できる方法や装置であればいずれでも良く、特に制限されないが紡糸口金の下に冷却風吹き付け筒などの冷却風吹き付け装置を設けておいて、紡出されてきた繊維に冷却風を吹き付けてガラス転移温度以下に冷却するのが好ましい。その際に冷却風の温度や湿度、冷却風の吹き付け速度、紡出糸条に対する冷却風の吹き付け角度などの冷却条件も特に制限されず、口金から紡出されて来た糸条の糸揺れなどを生じないようにしながら速やかに且つ均一に冷却できる条件であればいずれでも良い。そのうちでも、冷却風の温度を約20～30℃、湿度を20～60%、吹き付け速度を0.4～1.0m/secとして、紡出糸条に

対する冷却風の吹き付け方向を紡出方向に対すして垂直にして冷却するのが高品質繊維を円滑に得る点から好ましい。また冷却風吹き付け筒を用いて前記の条件で冷却を行う場合には、繊維化する繊維形成性重合体の種類に応じて紡糸口金の直下にやや間隔をあけてまたは間隔をあけないで、長さが約50～200cm程度の冷却風吹き付け筒を配置するのが好ましい。

【0021】次にガラス転移温度以下まで冷却した繊維糸条を引きつづいてそのまま直接加熱帯域に導入して延伸する。加熱帯域の温度は繊維化する繊維形成性重合体の種類に応じて異なり得るが、一般にはガラス転移点温度以上が良い。例えばポリエステルの場合には、ガラス転移温度より40℃以上高い温度としておくと、得られたポリエステル繊維の物性を実用上満足のゆくものとするので好ましく、100℃以上とするのが良い。加熱帯域の上限温度は、加熱帯域内での繊維間の融着や糸切れ、単糸切れなどが生じないような温度であれば良い。加熱帯域の種類や構造は、加熱帯域を走行する繊維を加熱帯域内の加熱手段などに接触せず加熱することができ、しかも加熱帯域内を走行する糸条とそれを包囲する空気との間に抵抗を生じさせて糸条張力を増大させて、繊維に延伸を生じさせることのできる構造であればいずれでも良い。加熱帯域の紡糸口金からの設置位置、加熱帯域の長さなどは、繊維化する繊維形成性重合体の種類や紡出量、冷却温度、紡糸速度、加熱帯の温度等により適宜調節できるが、紡糸口金直下から加熱帯域の入口までの距離を0.5～3m程度とし、加熱帯域の長さを1.0～2.0m程度としておくと、加熱帯域内で繊維を加熱して均一に円滑に延伸することができるので望ましい。

【0022】そして、加熱帯域で延伸された繊維に対して、必要に応じて油剤を付与してから、高速で引きとる。本発明では、上記した一連の工程からなる延伸した繊維の製造工程を、繊維の引取速度を4000m/分以上にして行うことも必要である。引取速度が4000m/分未満であると加熱帯域において繊維の延伸が充分に行われなくなり、得られる繊維の機械的物性が低下し、しかも上記した一連の工程からなる本発明の方法が円滑に行われず、特に加熱帯域における糸条の張力変動、過加熱などが生じて均一な延伸が行われにくくなる。尚本発明の繊維化方法により従来の方法に比べ延伸糸でありながら非晶部のルーズな繊維微細構造を有し、結果として繊維内部での金属イオンの移動を促進させ本発明の効果を発現する。

【0023】また本発明では、繊維の断面形状なども特に制限されない。通常の丸断面だけでなく、例えば楕円形、三角形、方形、多角形、中空形、多環形、アレイ形、V字形、T字形などの異形断面であっても良い。更に同種繊維形成性重合体あるいは異種繊維形成性重合体とのコンジュゲート繊維であってもよく、その断面は芯

7
絹、サイドバイサイド等特に制限されない。ただしコン
ジュゲート繊維の場合、抗菌性無機微粒子を含有した繊
維形成性重合体が繊維表面に少なくとも数%以上露出し
ている必要がある。抗菌性無機微粒子を含んだ繊維形成
性重合体が繊維表面に全く露出せず抗菌性無機微粒子を
含んでいない繊維形成性重合体に完全に包みこまれた断
面を有する繊維の場合は、著しく抗菌性能が低下するた
め実用面で抗菌性能の物足りないものとなる。

【0024】また本発明の抗菌性繊維は種々の菌類に対
して有効であり、例えば黒カビ、青カビ、枯草菌、緑膿
菌、大腸菌、腸炎ビブリオ菌、サルモネラ菌、白癬菌、
肺炎桿菌、MRSAなどに対して有効に使用することが
できる

【0025】そして本発明の繊維は、上着、肌着、ネマ
キ、腹巻き、作業服、エブロンなどの衣類、靴中敷、靴
下、カーペット、モップ用糸、ダスコンマット、フト
ン、フトンカバー、マクラカバー、ベッド、ベッドカバ
ー、毛布、シーツ、バスマット、タオル、キャビネット
タオル、テーブルクロス、カーテン、シャワーカーテ
ン、ネット、ドアノブカバー、壁紙、白衣、手術用縫
糸、手術衣、病衣、包帯、貼付剤基布、帽子、ガーゼ、
マスク、床擦れ防止マット、おむつカバー、紙おむつ、
カルテ用紙、スリッパ、ティッシュペーパー、ウェット
ティッシュ、歯ブラシ、手袋、各種ワイパー、エアコン
や空気清浄器および浄水器等のフィルター、食品用容器
などの種々の製品に使用することができ、耐久性のある
良好な抗菌性をそれらの製品に付与することができる。

【0026】

*【実施例】以下、実施例により本発明を詳細に説明する
が、本発明はこれらの実施例により何等限定されるもの
ではない。尚実施例中の測定値は以下の方法により測定
されたものである。

【0027】〈抗菌性試験〉実施例あるいは比較例で得
られた繊維を用い下記に示すHL(洗濯)処理方法で所定
回数洗濯した後、繊維製品衛生加工協議会で定めたシェ
ークフラスコ法に準拠して、試験菌として肺炎桿菌を用
いて、その滅菌率を下記式(1)により求めた。

10 滅菌率(%) = $\{(N_0 - N_1) / N_0\} \times 100$ (1)

N₀: 繊維に施した肺炎桿菌の数

N₁: 抗菌性試験終了時に繊維中で生存していた肺炎桿
菌の数

HL(洗濯)処理: 繊維を温度40℃の水40リットルを入
れた洗濯機に投入して、中性洗剤80gを加えて、5分間洗
濯した後、すすぎを3回行い、脱水乾燥する処理を1回の
洗濯とする。

【0028】実施例1

20 抗菌性無機微粒子として銀イオンを保持させたリン酸ジ
ルコニウム(平均粒径0.2μm、イオン交換率90%)を
2重量%添加した極限粘度[η]=0.68のポリエチ
レンテレフタレートを繊維化するにあたり、紡糸温度2
85℃、チューブヒーター温度200℃、引取速度45
00m/分とし、工程性良く7.5d/36fの延伸糸を
得た(表1、表2)。その結果、表2に示した通り良好な抗
菌性とその耐久性が確認された。

【0029】

【表1】

	銘柄 (d/f)	抗菌性無機微粒子					繊維 形態	配合比	繊維形成性 重合体
		基 材	粒径 (μm)	銀イオン 交換率 (%)	添加量 (wt%)				
実施例1	75/36	リン酸ジルコニウム	0.2	Ag	90	2	単糸	—	PET
実施例2	"	"	"	"	90	5	"	—	"
実施例3	50/36	"	"	Ag+Cu	95	3	"	—	"
実施例4	"	"	"	Ag+Zn	85	5	"	—	"
実施例5	"	"	"	Ag	80	2	"	—	ナイロン
実施例6	75/36	ゼオライト	1.0	"	"	2	"	—	PET
実施例7	"	リン酸ジルコニウム	0.2	"	"	2 (秤成分中)	芯/鞘	1/1	芯 PET 鞘 ナイロン
実施例8	"	ゼオライト	1.0	"	"	3 (PET中)	糸/糸 (1/1)	1/1	PET/ ナイロン
比較例1	"	リン酸ジルコニウム	0.2	"	"	0.1	単糸	—	PET
比較例2	"	"	"	"	"	15	"	—	"
比較例3	"	"	"	"	"	2	"	—	"
比較例4	"	"	"	"	"	3 (芯成分中)	芯/鞘	1/1	芯 PET 鞘 ナイロン
比較例5	"	"	"	"	"	3	"	—	PET

【表2】

	紡糸条件			工 程 性	濾過率			備 考
	紡糸温度 (°C)	フィラメント 温度(°C)	引取速度 (m/分)		乾 濾 10回後	洗 濾 50回後	乾 濾 150回後	
実施例1	285	200	4500	○	99	95	88	
実施例2	"	"	5000	○	99	98	92	
実施例3	280	180	"	○	99	90	80	
実施例4	"	200	"	○	99	92	80	
実施例5	260	180	4800	○	99	99	95	
実施例6	285	200	4000	○	99	90	85	
実施例7	280	"	"	○	99	95	90	
実施例8	"	180	4600	○	99	95	90	
比較例1	285	200	"	○	85	40	—	
比較例2	"	"	"	X	—	—	—	
比較例3	"	"	3400	△	—	—	—	物性不良
比較例4	"	"	4000	○	10	5	—	
比較例5	"	2ステップ法	"	○	99	80	50	

【0030】実施例2～4

抗菌成分の種類及び繊維中への抗菌性無機微粒子の添加量を変化させたこと以外は実施例1と同要領で製糸化し、いずれも工程性よく75d/36f及び50d/36fの延伸糸を得た(表1、表2)。そのときの抗菌性評価結果を表2に示した。

【0031】実施例5

繊維形成性重合体としてナイロンを使用したこと以外は、実施例1と同要領で製糸化し、工程性良く50d/36fの延伸糸を得た(表1、表2)。そのときの抗菌性評価結果を表2に示した。

【0032】実施例6

抗菌性無機微粒子の基材としてゼオライトを用いたこと以外は、実施例1と同要領で製糸化し工程性よく75d/36fの延伸糸を得た(表1、表2)。そのときの抗菌性評価結果を表2に示した。

【0033】実施例7

芯に $[\eta] = 0.68$ のポリエチレンテレフタレート、鞘に銀イオンを保持させたリン酸ジルコニウムを2重量%添加した分子量13000のナイロン6を用いた芯鞘型複合繊維とすること以外は実施例1と同要領で製糸化し、工程性良く75d/36fの延伸糸を得た(表1、表2)。そのときの抗菌性評価結果を表2に示した。

【0034】実施例8

銀イオンを保持させたゼオライトを3重量%添加した $[\eta] = 0.68$ のポリエチレンテレフタレートと分子量13000のナイロン6とサイドバイサイド型に配すること以外は実施例1と同要領で製糸化し、工程性良く75d/36fの延伸糸を得た(表1、表2)。そのときの抗菌性評価結果を表2に示した。

【0035】比較例1

抗菌性無機微粒子として銀イオンを保持させたリン酸ジルコニウムをポリエチレンテレフタレート中に0.1重量%添加したこと以外は実施例1と同要領で製糸化した(表1、表2)。工程性は良好だったが抗菌性能は実施例1に比べて悪かった。

【0036】比較例2

抗菌性無機微粒子として銀イオンを保持させたリン酸ジルコニウムをポリエチレンテレフタレート中に15重量%添加したこと以外は実施例1と同要領で製糸化を試みたが、ポリエチレンテレフタレートの粘度低下が大きく曳糸性が乏しいため満足な工程性が得られなかった(表1、表2)。

【0037】比較例3

紡糸速度を3400m/分としたこと以外は実施例1と同要領で製糸化を試みたが延伸斑を生じ、断糸が多く、物性も伸度が大きく実用性に乏しいものとなった(表1、表2)。

【0038】比較例4

芯に銀イオンを保持させたリン酸ジルコニウムを3重量%添加した $[\eta] = 0.68$ のポリエチレンテレフタレート、鞘に分子量13000のナイロン6を用いた芯鞘型複合繊維とすること以外は実施例7と同要領で製糸化した(表1、表2)。工程性は良好であったが抗菌性能は実施例1に比べて著しく劣るものとなった。

【0039】比較例5

抗菌性無機微粒子と繊維形成性重合体は、実施例1と全く同様とし製糸化方法は1000m/分で一旦巻取り、その後別工程にて延伸処理を施す従来法(2ステップ法)にて75d/36fの延伸糸を得た(表1、表2)。工程性は良好であり、抗菌評価も初期性能は優れていたが、耐久性の面で本発明より劣るものであった。

【0040】以上、本発明においては工程性・抗菌性能及びその耐久性は極めて良好であった。しかしながら比較例で示した通り、抗菌成分が少なすぎると効果が不十分であり、抗菌成分量を増加すると工程性を悪化させる。また抗菌成分が繊維表面に出ていないとその効果は乏しい。更に従来の製糸法においても抗菌性能の耐久性はある程度認められるが本発明の製糸法により得られる抗菌性繊維の方が耐久性が一段と向上することが分かった。